

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-041303

(43)Date of publication of application : 13.02.1996

(51)Int.Cl.

C08L 67/02
B29C 45/00
C08J 5/00
C08L 69/00
G11B 7/24
// C08G 63/197

(21)Application number : 06-197301

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(22)Date of filing : 28.07.1994

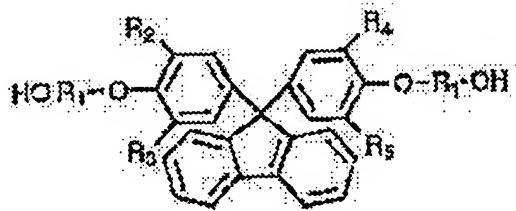
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(54) RESIN COMPOSITION FOR OPTICAL MATERIAL AND PREPARATION THEREOF

(57)Abstract:

PURPOSE: To prepare a resin compsn. for an optical material having excellent transparency, moisture resistance, mechanical strength, and dimensional and form stability by blending a particular linear polyester polymer with an arom. polycarbonate.

CONSTITUTION: A resin compsn. comprising a homogeneous blend of a linear polyester polymer comprising an arom. dicarboxylic acid or a diester deriv. thereof, a dihydroxy compd. represented by the formula, and a 2-4C aliph. glycol with an arom. polycarbonate. In the formula, R1 is a 2-4C alkyl; and R2, R3, R4, and R5 are each H or a 1-4C alkyl. The glass transition temp. of the resin compsn. should be 78°C or above, pref. 80°C or above. A glass transition temp. below 78°C results in, for example, deformation of a substrate during the storage of an optical disk product, thus posing a problem such as occurrence of a noise.



LEGAL STATUS

[Date of request for examination] 14.08.1996

[Date of sending the examiner's decision of rejection] 17.11.1998

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3023279

[Date of registration] 14.01.2000

[Number of appeal against examiner's decision of rejection] 10-019593

[Date of requesting appeal against examiner's decision of rejection] 16.12.1998

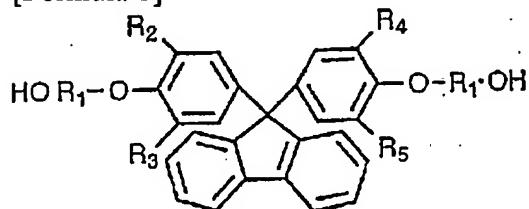
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CLAIMS

[Claim(s)]

[Claim 1] Aromatic series dicarboxylic acid or its diester derivative, and a general formula (1)

[Formula 1]



For the alkyl group of carbon numbers 2-4, R2, R3, R4, and R5, (R1 is the dihydroxy compound independently shown by alkyl group) of hydrogen or carbon numbers 1-4, and a resin constituent for optical materials with which a carbon atomic number consists of an aliphatic series glycol of 2 to 4 and which consists of a linear polyester polymer and uniform blend mixture with an aromatic series polycarbonate substantially.

[Claim 2] Aromatic series dicarboxylic acid or its diester derivative, and a general formula (1)

[Formula 1] R1 -- the alkyl group of carbon numbers 2-4, R2, R3, and R4 -- And R5 On the dihydroxy compound independently shown by hydrogen or the alkyl group of carbon numbers 1-4, and the real target with which a carbon atomic number consists of an aliphatic series glycol of 2 to 4, the polyester polymer on a line (the first component), The manufacturing method of the optical material characterized by injection molding the base material which consists of uniform blend mixture with an aromatic series polycarbonate (the second component).

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the resin for optical materials, this invention is small and a birefringence is excellent in transparency, moisture resistance, a mechanical strength, and a dimension and gestalt stability, and especially, an information signal is recorded on the board and it is related with the resin for optical disk substrates suitable to reproduce and economical.

[0002]

[Description of the Prior Art] The application has expanded quickly voice, the image, and the optical disk that records and reproduces information by detecting the detailed signal on a disk substrate in recent years using laser light. The record on this optical disk substrate needs submicron to be precision and its to be dimensional stability, for preservation stability to be still better, etc. Moreover, it is required as an optical property for the transparency of a substrate to be good and for a birefringence to be small. For this reason, the actual condition is that these products are quite a large sum.

[0003] Conventionally, as such an optical disk substrate, transparency plastic material, such as polymethylmethacrylate (PMMA), a polycarbonate (PC), and amorphous polyolefine (APO), is used. Moreover, special aromatic polyester copolymerization resin (JP,57-208645,A, JP,2-98845,A, 2-38428 official report) is proposed.

[0004] However, although PMMA shows a good property in respect of an optical property, hygroscopicity is large, a disk substrate absorbs the moisture in air, it is easy to come out of a camber, and it has a fault with scarce thermal resistance the top whose dimensional stability is not good. moreover, although PC of hygroscopicity is low and there are few cambers, a fluidity is bad, and there is a problem of difficulty in a moldability, and a birefringence also has a fault of imperfection. Furthermore, although APO has the outstanding optical property, it is very expensive.

[0005] What is depended on JP,57-208645,A which proposed aromatic polyester copolymerization resin, JP,2-98845,A, and a 2-38428 official report on the other hand is necessarily unsatisfying, and using an expensive raw material. [that an optical property is inadequate] [that thermal resistance runs short]

[0006] That is, and transparency is good, a birefringence is small and a moldability is good, it excels in thermal resistance and development of an advantageous optical disk substrate is desired economically.

[0007]

[Problem(s) to be Solved by the Invention] The place which completes a header and this invention and sets it as the object that the substrate for optical disks which was excellent when this invention persons cast the blend mixture of the polyester copolymer and the polycarbonate which has a specific presentation, as a result of repeating research wholeheartedly in view of many above-mentioned troubles is obtained has a small birefringence, it is excellent in transparency, moisture resistance, a mechanical strength, and a dimension and gestalt stability, and is to offer the heat-resistant good resin for optical disk substrates. Effectiveness will be made clear from the following explanation at other object lists of this invention.

[0008]

[Means for Solving the Problem] The above-mentioned object is aromatic series dicarboxylic acid or its diester derivative, and a general formula (1).

[Formula 1] R1 -- the alkyl group of carbon numbers 2-4, R2, R3, and R4 -- And R5 On the dihydroxy compound independently shown by hydrogen or the alkyl group of carbon numbers 1-4, and the real target with which a carbon atomic number consists of an aliphatic series glycol of 2 to 4, the polyester polymer on a line (the first component), It is attained by the resin constituent for optical materials which consists of uniform blend mixture with an aromatic series polycarbonate (the second component), and its manufacture approach.

[0009] the polymerization degree of the aromatic series polycarbonate (the second component) used for this blend although the two above components are blended and the resin for optical materials is constituted -- intrinsic viscosity (it measures at 20 degrees C among 60 % of the weight of phenols, and the mixed solution of 40 % of the weight of 1,1,2,2-tetrachloroethane) -- carrying out -- 0.2 -- or it is 0.3 thru/or 0.55 preferably about 0.7. A mechanical strength when intrinsic viscosity fabricates

the object of under this range to a disk substrate is inadequate. Moreover, the object with which intrinsic viscosity exceeds this range reduces the fluidity at the time of fabricating, it becomes easy to carry out molecular orientation, and a birefringence becomes large after injection molding.

[0010] Moreover, polymerization degree of the above-mentioned polyester polymer (the first component) is made into intrinsic viscosity, does not have 0.3, and is 0.35 thru/or about 0.7 preferably about 0.8. A mechanical strength when intrinsic viscosity fabricates the object of under this range to a disk substrate is weak. Moreover, the fluidity at the time of fabricating the object with which intrinsic viscosity exceeds this range falls, a cycle property is reduced, and the rate of a birefringence of mold goods tends to become large.

[0011] The resin constituent of this invention gives a desirable single glass transition temperature, when a differential scanning calorimetry (DSC) is performed. Generally, although two peaks corresponding to a polyester polymer (the first component) and an aromatic series polycarbonate (the second component) and the other peak, and a shoulder may be given, the many have bad transparency, it is thermally unstable, a moldability is also bad, and a good optical material cannot become easily.

[0012] 80 degrees C or more 78 degrees C or more are preferably required for the glass transition temperature of the resin constituent of this invention. When glass transition temperature is less than 78 degrees C, an optical disk product is under preservation, a base deforms, and problems, such as noise generating, arise.

[0013] although the resin constituent for optical materials of this invention blends two components with each above-mentioned degree of polymerization and it is constituted -- the rate of a blend -- the weight ratio of a polyester polymer (the first component) and an aromatic series polycarbonate (the second component) -- it is -- 5:95-90:10 -- the range of 10:90-80:20 is preferably suitable. The effectiveness that the rate of a blend of a polyester polymer (the first component) reduces the rate of a birefringence under in this range is not enough.

[0014] In this invention, aromatic series dicarboxylic acid has especially a desirable terephthalic acid, although a terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, etc. are mentioned.

[0015] The dihydroxy compound expressed with a general formula (1) in this invention is [-(4-hydroxy ethoxy phenyl)- A fluorene is desirable.] 9 and 9-screw. -(4-hydroxy ethoxy phenyl)- It is fluorene, 9, and 9-screw. -(4-hydroxy propoxy phenyl)- It is fluorene, 9, and 9-screw. -(4-hydroxy butoxy phenyl)- Although there is a fluorene etc., it is 9 and 9-screw especially.

[0016] 9 and 9-screw -(4-hydroxy ethoxy phenyl)- A fluorene is 9 and 9-screw. -(4-hydroxyphenyl)- Ethyleneoxide (following, EO) is added to a fluorene and it is obtained. under the present circumstances, everything but 2EO adduct (9 and 9-screw -(4-hydroxy ethoxy phenyl)- fluorene) which one molecule of ethyleneoxides added at a time to both the hydroxyl groups of a phenol -- further -- impurities added to the overchild several minutes, such as 3EO adduct and 4EO adduct, may be contained When impurities, such as 3EO(s) and 4EO, increase in number, the thermal resistance of a polyester polymer is made to fall. Although there should just be 85% or more of purity of 2EO adduct at this time, it is 95% or more preferably.

[0017] 9 and 9-screw -(4-hydroxy propoxy phenyl)- Fluorene, 9, and 9-screw -(4-hydroxy butoxy phenyl)- A fluorene is 9 and 9-screw. -(4-hydroxyphenyl)- It will be obtained if 3-chloro-propane-1-oar and 4-chloro-propane-1-oar are made to react to a fluorene under alkaline conditions respectively. It is 95% or more preferably that there should just be purity in this case at 85% or more.

[0018] In this invention, as an aliphatic series glycol, although ethylene glycol, 1,3-propanediol, 1, 2-propanediol, 1,4-butanediol, 1, 2-butanediol, and 1,3-butanediol are mentioned, especially, ethylene glycol and 1,4-butanediol are desirable and especially ethylene glycol is desirable.

[0019] In this invention as an aromatic series polycarbonate For example, although the polycarbonate which is made to carry out the interfacial polymerization of the 2 and 2-screw-(4'-hydroxyphenyl) propane (henceforth "bisphenol A") by the phosgene and the alkali water-solution-methylene chloride system as aromatic series diol, and is obtained is raised As other aromatic series diols, for example, screw-(4-hydroxyphenyl) methane, A 1 and 1-screw-(4'-hydroxyphenyl) ethane, 1, and 1-screw-(4'-hydroxyphenyl) propane, A 2 and 2-screw-(4'-hydroxyphenyl) butane, 2, and 2-screw-(4'-hydroxyphenyl) pentane, A 2 and 2-screw-(4'-hydroxyphenyl) isopentane, 2, and 2-screw-(4'-hydroxyphenyl) hexane, A 2 and 2-screw-(4'-hydroxyphenyl) isohexane, 4, and 4'-dihydroxy triphenylmethane color, A 4 and 4'-dihydroxy tetraphenylmethane, 1, and 1-screw-(4'-hydroxyphenyl) cyclohexane, A 2 and 2-screw-(4'- hydroxy-3' methylphenyl) propane, A 2 and 2-screw-(4'- hydroxy-3', 5'-dimethylphenyl) propane, Dihydroxy diphenyl ether, dihydroxy diphenylsulfone, A kind chosen from the phenolic compound of bivalence, such as bisphenols called a dihydroxydiphenyl sulfide and hydroquinone, resorcinol, o-methyl resorcinol, and o-cumyl resorcinol, or two sorts or more may be used.

[0020] Although there is a melting kneading approach by the extruder, a kneader, etc. or the solution blend approach which mixes the two above-mentioned component in the condition of having made it dissolving in common good solvents, such as a methylene chloride, as the blend approach of the two above-mentioned component, especially this is not limited, and if it is the polymer blend approach usually used, it may use what kind of approach.

[0021] In this invention, from well-known approaches, such as melting polymerization methods, such as for example, an ester interchange method and a direct polymerization method, a solution polymerization method, and interfacial polymerization, the polyester polymer (the first component) with which the dihydroxy compound shown by aromatic series dicarboxylic acid, or its diester derivative and general formula (1) and a carbon atomic number consist of an aliphatic series glycol of 2 to 4 chooses a proper approach, and can be manufactured. Moreover, a well-known approach can be used as usual also about reaction conditions, such as a polymerization catalyst in that case.

[0022] In this invention, the polyester polymer (the first component) is good, especially when using a melting polymerization method. Namely, 9 and 9-screw -(4-hydroxy ethoxy phenyl)- An end group is the property which resembled aliphatic series glucohol well, and the compound of a fluorene has high reactivity. This is 9 and 9-screw. -(4-hydroxyphenyl)- Compared with a fluorene, it differs remarkably.

For this reason, the manufacture approach which does not need to use a raw material called an acid chloride, therefore chlorine does not mix in essence is possible, the amount of the catalyst used could be lessened in the reaction condition in high temperature, and few approaches of a residual foreign matter became possible.

[0023] In this invention, in order to manufacture a polyester polymer (the first component) by the ester interchange method of a melting polymerization method, as for the dihydroxy component expressed with a general formula (1), it is desirable that it is [ten to 95 of glycol component in resin mol] %. If this increases more than 95-mol %, a melting polymerization reaction will not progress or it will not reach sufficient polymerization degree. When [than 95 mol %] more, it manufactures by the solution polymerization method or interfacial polymerization.

[0024] Although acid chloride is generally used as active species of an acid component or a methylene chloride, chloroform, etc. use it as a solvent in this invention in adopting a solution polymerization method, interfacial polymerization, etc. in case a polyester polymer (the first component) is manufactured In a polymer, the chloride and catalyst compound which are a by-product remain, and since the quality top of a product of this thing generally is not good, generally a residual foreign matter must be removed after a polymerization process. These reduce the operability in forming cycles, such as a sheet, a film, a plate, and fiber, and also reduce the quality of the Plastic solid acquired. For example, a pyrolysis occurs so much at the time of heating at high temperature.

[0025] Moreover, since the reflective film and record film will be corroded and the life and dependability of an optical disk or a magneto-optic disk will be reduced if the amount of residual chlorine is in a substrate although metal thin films, such as reflective film and record film, are fixed by approaches, such as vacuum evaporationo and sputtering, to a substrate in case the resin constituent of this invention is used as optical materials, such as an optical disk and a magneto-optic disk, the process which removes the chlorine which remains [filtration / sufficient washing filtration, etc.] is needed. The ester interchange method which chlorine does not mix as a polymerization method of a polyester polymer (the first component) is more desirable.

[0026] An injection-compression-molding machine usually suits shaping of an optical disk substrate well, and metal mold skin temperature and resin temperature are important in especially a process condition. Although a presentation, polymerization degree, etc. of a dihydroxy component cannot generally prescribe, metal mold skin temperature has 50 degrees C or more desirable 160 degrees C or less, and the resin temperature at this time is good to make it 250-degree-C or more become 350 degrees C or less. When [neither of] metal mold skin temperature is 250 degrees C or less, the fluidity of resin and imprint nature are bad, and since stress distortion remains at the time of injection molding, and there is an inclination for the rate of a birefringence to become large and a molding cycle is also prolonged, it is economical. Although imprint nature is good when a die temperature is 160 degrees C or more, it is easy to deform at the time of mold release. Moreover, since disassembly of resin tends to take place and it becomes the cause of lowering of mold goods on the strength, and coloring when resin

temperature is 350 degrees C or more, it is not desirable.

[0027] When fabricating an optical material from the resin constituent for optical materials of this invention, at the process which begins the charge process of a raw material, extrudes a polymerization reaction and a copolymer in a refrigerant, and is made into the shape of a pellet type or a sheet, to carry out by taking care so that dust etc. may not enter is desired. In for compact disks, this air cleanliness class is usually 1000 or less, and, in for still more advanced information record, is 100 or less.

[0028]

[Example] An example is given below and this invention is explained concretely.

The example Naka "section Weight % is meant for a certain *****%"."

Moreover, the intrinsic viscosity, the glass transition temperature, the rate of a birefringence, and light transmittance of the polymer in an example were measured with the measuring method shown below.

[0029] (1) Copolymers 0.15-0.5g were measured at 80 degrees C, viscosity was measured to 50ml of mixed solutions of 60 % of the weight of intrinsic-viscosity phenols of a polymer, 1, 1, 2 and 2, and 40 % of the weight of - tetrachloroethanes at 20 degrees C after the dissolution, and it was decided that it would be them.

[0030] (2) It heated and measured with the programming rate of 10 degrees C / min using about 10mg of samples which quenched after using the glass-transition-temperature differential scanning calorimeter (physical science electrical-and-electric-equipment DSC-8230) and heat-treating about 170 degrees C for 10 minutes beforehand. JIS K 7121-1987 As it defined, glass-transition-temperature T_{mg} and the extrapolation glass-transition-temperature termination temperature T_{eg} were searched for.

[0031] (3) With the rate KARUTSU ice company nature polarization microscope of a birefringence, it equipped with SERARUMON, BEREKKU, and a brace KERA type compensator, and measured by the 546nm homogeneous light.

[0032] (3-1) Assessment ***** in a film was produced at 260-300 degrees C, the disc-like test piece with a diameter [of 30mm] and a thickness of 1mm was produced by melting and extrusion molding, press forming of the shaping test piece was further carried out at 160-240 degrees C, and the film with a thickness of 80-150 micrometers was obtained. The obtained film was cut down 4x40mm in the shape of a strip of paper, and the measurement test piece was obtained.

Extrapolation glass transition termination temperature At T_{eg}+1 degree C temperature, the measurement test piece was quenched after 40% drawing by 10%/sec, and the oriented film was obtained. The rate of a birefringence of these films was measured.

[0033] (3-2) The retardation of the location of 50mm of radial was measured from the core of the disk with 1.2mm [in thickness], and a diameter of 120mm fabricated with the assessment injection-compression-molding machine in a disk.

[0034] (4) Light transmittance with a wavelength of 500nm was measured with the spectrophotometer using the light transmittance disk base sample.

[0035] (Preparation of a polyester copolymer)

(Component 1-1) Dimethyl terephthalate 38 sections, 9, and 9-screw -(4-hydroxy ethoxy phenyl)- Fluorene The 35 sections, ethylene glycol The 27 sections are used

as a raw material and it is calcium acetate as a catalyst. Having supplied these to the reaction vessel and stirring them using the 0.042 sections, according to the conventional method, it heated gradually at 230 degrees C from 190 degrees C, and the ester exchange reaction was performed. Germanium dioxide which is a polymerization catalyst after extracting the methanol of the specified quantity out of a system It is trimethyl phosphate in order to prevent coloring with the 0.012 sections. The 0.033 sections are supplied, performing reduced pressure gradually with temperature up, and extracting the ethylene glycol to generate, 280 degrees C is reached in whenever [heating tank temperature], and a degree of vacuum is made to reach 1 or less Torr. This condition was maintained, waiting and the reaction after 2-hour progress were ended for lifting of viscosity, and the polyester polymer was obtained.

[0036] The intrinsic viscosity of this polyester polymer was 0.55, and glass transition temperature was 124 degrees C. 9 and 9-screw [as opposed to the terephthalic-acid component of this polyester polymer by measurement of 1 H-NMR spectrum] -(4-hydroxy ethoxy phenyl)- The percentage of a fluorene component was 40%.

[0037] (Component 1-2) It is dimethyl terephthalate about a raw material presentation. 26 sections, 9, and 9-screw -(4-hydroxy ethoxy phenyl)- Fluorene The 56 sections, ethylene glycol It considers as the 18 sections and they are the 0.028 sections and a germanium dioxide about calcium acetate. The 0.009 sections, trimethyl phosphate It changed into the 0.022 sections, and also the process was advanced similarly, and the pellet was obtained.

[0038] The intrinsic viscosity of this polyester polymer was 0.51, and glass transition temperature was 146 degrees C. 9 and 9-screw [as opposed to the terephthalic-acid component of this polyester polymer by measurement of 1 H-NMR spectrum] -(4-hydroxy ethoxy phenyl)- The percentage of a fluorene component was 80%.

[0039] (Component 2) The bisphenol A polycarbonate resin of the commercial grade for optical disks was used as (a component 2). The intrinsic viscosity of this resin was 0.43.

[0040] (Example 1) The component (1-1) and the component (2) were blended at a rate of 30:70 (polymerization ratio), and the pellet was created using the extruder. The result of the differential scanning calorimetry (DSC) of this resin constituent is shown in drawing 1. They were a single glass transition temperature and 134.3 degrees C.

[Drawing 1]

[0041] After injection molding resin at 290 degrees C and obtaining a disc-like sample, it pressed at 250 degrees C and the film with a thickness of 130micro was obtained. When extended at 140 degrees C, the rate of a birefringence was 41×10^{-4} . Moreover, the molding shrinkage for which it asked using the test piece injection molded and obtained with the die temperature of 100 degrees C and the resin temperature of 310 degrees C was 0.69, and the bending elastic modulus was 2.5×10^4 Kgf/cm². The retardation of the disk which carried out injection molding on the same conditions was 13nm, and light transmittance was 90%.

[0042] (Examples 2-3) The component (1-1) and the component (2) were blended at

a rate of 50:50 and 70:30 (weight ratio), and ** let was created using the extruder. The result which measured like (the example 1) and was obtained is shown in a table 1.

[A table 1]

	組成 (%)		ガラス転移温度 (°C)		複屈折率 (フィルム)	成形収縮率 (%)	曲げ弾性率 (10 ⁴ *Kgf/cm ²)	レターデーション (ディスク) (nm)	光透過量 (%)
	組成 (#1)	組成 (#2)	T _{mg}	T _g					
実施例1	40	30	134	139	41*10 ⁻⁴	0.69	2.5	13	90
実施例2	40	50	129	134	28*10 ⁻⁴	0.69	2.5	11	90
実施例3	40	70	126	130	18*10 ⁻⁴	0.71	2.2	9	90
実施例4	80	20	132	136	28*10 ⁻⁴	0.71	2.7	11	90
比較例1	—	0	140	147	168*10 ⁻⁴	0.57	2.7	30	90

(#1) (第一成分) 中の一般式 (1) で表されるジヒドロキシ成分の割合。

(#2) 树脂組成物中の (第一成分) のブレンド率。

[0043] (Example 4) The component (1-2) and the component (2) were blended at a rate of 20:70 (weight ratio), and ** let was created using the extruder. The result which measured like (the example 1) and was obtained is shown in a table 1.

[0044] (Example 2 of a comparison) After carrying out melting shaping of the polycarbonate resin (component 2) of the commercial grade for optical disks at 300 degrees C and obtaining the sample on a disc, it pressed at 240 degrees C and the film with a thickness of 120 micrometers was obtained. When extended at 148 degrees C, the rate of a birefringence was 168x10⁻⁴.

[0045] Moreover, the molding shrinkage for which it asked using the test piece injection molded and obtained with the die temperature of 100 degrees C and the resin temperature of 310 degrees C was 0.57, and the bending elastic modulus was 2.7*10⁴ Kgf/cm². The retardation of the disk which carried out injection molding on the same conditions was 30nm, and light transmittance was 90%.

[0046] The polycarbonate resin (example 1 of a comparison) generally used is understood that an optical anisotropy is large like [it is ***** and] from a comparison with a table 1.

[0047]

[Effect of the Invention] As stated above, the resin constituent for optical materials of this invention has transparency and good thermal resistance, and it is the optical material excellent in a moldability, dimensional stability, and chemical resistance. Furthermore, the optical disk substrate which consists of this resin constituent has industrially useful optical anisotropy small.

[Translation done.]